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(54) Title of the Invention: Multilayer coinjection
stretch blow molded
15 plastic container

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Specification

5

1. TITLE OF THE INVENTION

Multilayer coinjection stretch blow molded
plastic container

2. CLAIMS

10 (1)

A multilayer coinjection stretch blow molded
plastic container comprising inner and outer surface
layers of a thermoplastic polyester (D) and an
intermediate layer, the intermediate layer including
15 a composition (C) having a blend of 5 to 40 parts by
weight of an ethylene-vinyl acetate copolymer or a
saponified resin of the ethylene-vinyl acetate
copolymer (B), or both, that satisfies the following
formulae (I) to (IV), and 100 parts by weight of a
20 saponified ethylene-vinyl acetate copolymer (A) having
0.0002 to 0.2 mol % of a vinylsilane compound unit, 20
to 60 mol % of ethylene content, and a 95% or higher
saponification degree of the vinyl acetate component.

$$1 \leq \text{MI (B)} / \text{MI (A)} \leq 200 \quad (\text{I})$$

25 $\text{MP (B)} \leq \text{MP (A)} \quad (\text{II})$

$$\text{CH (A)} \leq \text{CH (B)} \quad (\text{III})$$

$$\text{DS (A)} \geq \text{DS (B)} \quad (\text{IV})$$

where MI(A) and MI(B) are melt indexes of the resins (A) and (B) respectively (2160 g, 190 °C) (g/10 min), MP(A) and MP(B) are melting points or softening points of the resins (A) and (B) respectively (°C),
5 CH(A) and CH(B) are contents of C₂H₄ in the resins (A) and (B) respectively (mole %), and DS(A) and DS(B) are saponification degrees of the resins (A) and (B) respectively (%).

(2)

10 The multilayer coinjection stretch blow molded plastic container according to claim 1, wherein the multilayer plastic container is heat-treated at a temperature given by the following formula (V).

$$(T_p - 20) > T_c > T_B \quad (V)$$

15 where T_p is a melting point of thermoplastic polyester (°C),

T_c is a heat treatment temperature for container (°C), and

T_B is a melting point or softening point of resin (B) (°C).

(3)

The multilayer coinjection stretch blow molded plastic container according to any one of claims 1 and 2, wherein the thermoplastic polyester (D) is a
25 composition containing 1 to 20 parts by weight of the resin (B) per 100 parts by weight of a thermoplastic polyester.

(4)

The multilayer coinjection stretch blow molded plastic container according to any one of claims 1 to 3, wherein the resin (B) is an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer, or both, that has been modified with maleic anhydride and the like, or a blend of 10 to 90 parts by weight of the modified copolymer and 90 to 10 parts by weight of an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer, or both.

3. DETAILED DESCRIPTION OF THE INVENTION

A. Field of Industrial Application

The present invention relates to a multilayer coinjection stretch blow molded plastic container made of synthetic resin that is excellent in gas barrier properties such as oxygen and carbonic acid gas, moisture resistance, aroma retention properties, flavor barrier properties, and appearance and is used for a container of drinks, food, cosmetics, and the like, and particularly to a multilayer coinjection stretch blow molded plastic container that is provided with a structure of at least three layers having thermoplastic polyester (hereinafter, abbreviated as PES) as inner and outer surface layers and a saponified ethylene-vinyl acetate copolymer (hereinafter, abbreviated as EVOH) composition as an intermediate layer and is greatly

improved particularly in resistance to interlayer delamination caused by impact.

B. Conventional Art

Polyester containers produced by a stretch blow molding method are used in a number of fields because of excellent transparency and rigidity thereof. However, gas barrier properties are not necessarily sufficient, and therefore storage of food and the like has been limited to a short period. To prevent this defect, various methods in which polyester is combined with an ethylene-vinyl alcohol copolymer having excellent gas barrier properties to form a multilayered structure have been proposed. That is, as techniques to produce preforms prior to stretch blowing, there are coextrusion molding technique, multi-step injection molding technique, coinjection molding technique, and the like, each of which has advantages and disadvantages. Among them, the coinjection molding technique is a technique currently drawing much attention because of the features that not only is the machine for coinjection molding simple but also this technique gives rise to a structure in which EVOH is completely covered with PES and provides an apparently excellent multilayered container owing to contact adhesion caused by atmospheric pressure even when no adhesive resin is present between EVOH and PET. However, when an impact is given to the container after filling food in practical

use, delamination occurs between PES and EVOH, posing a big problem to its appearance. Hence, the coinjection molding technique has been studied for a structure containing an adhesive layer (hereinafter, referred to as Ad) such as substrate/Ad/EVOH/Ad/substrate (JP-A No. 501040/1981), substrate/Ad/EVOH/Ad/substrate/Ad/EVOH/Ad/substrate (JP-A No. 135169/1975, JP-A No. 152411/1986, JP-A No. 152412/1986, JP-A No. 259944/1986), or the like.

10 However, production facilities become very complicated, control of the thickness of each layer is often difficult, and this technique is in a situation inferior to those of other techniques such as coextrusion molding (pipe method) in view of production cost and productivity.

15 Another big problem lies in that it is often the case that impact delamination is not perfectly prevented even with a multilayer coinjection stretch blow molded container containing the above adhesive resin layer. That is, even when a container shows a relatively high

20 value of adhesion strength (T type peeling strength) of 400 to 600 g/10 mm breadth between PES and EVOH of the body portion of the container, there are cases that impact delamination is very easy to occur, whereas even when a container shows the adhesion strength as low as

25 20 to 40 g/10 mm breadth indicating little adhesion, there are cases that impact delamination is hard to occur compared with the container having the high adhesion

strength. Thus, since the cause of impact delamination remains uncertain, impact delamination poses a difficult problem, and its prevention is desired.

C. Problems to be Solved by the Invention

5 There was a problem that an impact to a coinjection stretch blow molded PES container that contains no independent adhesive resin layer but is laminated with EVOH as gas barrier resin causes delamination between PES layer and EVOH layer whether the container is an
10 empty container, a container filled at atmospheric pressure, or a container filled at high pressure, giving rise to a defect in appearance of the container. Accordingly, the present inventors conducted diligent research on a method of preventing the delamination.

15 D. Means for Solving the Problems

 The present inventors produced multilayer preforms having EVOH on inner and outer surface layers of PES or an intermediate layer in which PES and EVOH are completely enclosed by the inner and outer surface
20 layers and conducted diligent studies on the composition of EVOH with the aim of preventing interlayer delamination between the EVOH layer and the PES layer caused by impact on a container when the multilayer parison was stretch blow molded to produce the container.
25 As the result, when an EVOH composition (C) in which an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer (B), or both, that

satisfies the formulae (I) to (IV) below was blended with EVOH (A) containing vinyl compound unit was used and coinjection-molded, it was found that delamination of a container filled with water at atmospheric pressure or water under pressure that is caused by an impact was
5 hard to occur despite the fact that the adhesion strength (T type peeling strength) between the EVOH composition layer and the PES layer of the body portion of the container was as very low as ca. 30 to 100 g/10 mm breadth.
10 Further, when a modified copolymer of an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer that is obtained by grafting with maleic anhydride and the like, or a composition in which 90 to 10 parts by weight of an ethylene-vinyl acetate
15 copolymer or a saponified ethylene-vinyl acetate copolymer, or both were blended with 10 to 90 parts by weight of the modified polymer was used as the resin (B), the present inventors found that impact resistance was further greatly improved and perfected the present
20 invention. This fact is evident from the examples described below.

$$1 \leq MI(B) / MI(A) \leq 200 \quad (I)$$

$$MP(B) \leq MP(A) \quad (II)$$

$$CH(A) \leq CH(B) \quad (III)$$

$$25 \quad DS(A) \geq DS(B) \quad (IV)$$

where MI(A) and MI(B) are the melt indexes of the resins (A) and (B) respectively (2160 g, 190 °C) (g/10 min),

MP(A) and MP(B) are the melting points or softening points of the resins (A) and (B) respectively ($^{\circ}\text{C}$), CH(A) and CH(B) are the contents of C_2H_4 in the resins (A) and (B) respectively (mole %), and
5 DS(A) and DS(B) are the saponification degrees of the resins (A) and (B) (%).

Here, MP refers to melting temperature when an endothermic melting peak is present in DSC and to Vicat softening temperature when an endothermic peak is not
10 present.

A heat-set stretch blow molded container after a pipe produced by a 2 kind-3 layer coextrusion machine using the EVOH composition (C) and PET has been molded into a parison with bottom, or a stretch blown container
15 from a pipe using a 3 kind-5 layer coextrusion machine with the EVOH (A), the resin (B), and the PES sometimes shows a relatively high value of adhesion strength in the body portion of the container; nevertheless delamination due to an impact was found to easily occur.
20 That is, the fact that large impact delamination resistance is developed only when the above EVOH composition (C) was used in coinjection molding is unexpected, though the reason is uncertain. This fact is also evident from the examples described below.

25 In the present invention, it is not particularly necessary to provide an independent adhesive resin layer between (D) and (C), but it is an option to provide the

layer, for example, the layer having a thin thickness.

The coinjection stretch blow molded container with the above composition was found to show not only great improvement in impact delamination resistance but also
5 surprisingly great improvement in stripe-shaped irregularity in thickness of the EVOH layer that tends to occur in the body portion of the container and particularly in its bottom portion and mouth periphery. Generally, in coinjection and costretch process of PES
10 with EVOH, stretching irregularity, particularly stripe-shaped irregularity in the longitudinal direction of the bottle develops with ease, and thus defect in appearance tends to occur because EVOH is poor in stretchability compared with PES. Although the
15 reason why the stripe formation is greatly reduced when the EVOH composition (C) is used is unclear, it is inferred that the stretchability of the EVOH composition (C) was improved, compared with that of the EVOH (A), by blending the resin (B) with the EVOH (A) and that
20 an interaction of the EVOH composition (C) with the PES (D) was strengthened, contributing to the prevention of the occurrence of stripes. These facts are also evident from the examples described below.

25 E. More Detailed Description of the Invention

For the PES (D) used in the present invention, a condensation polymer having aromatic dicarboxylic acid

or alkyl ester thereof and glycol as main components is used, and PES mainly composed of ethylene-terephthalate is particularly preferred in order to achieve the object of the present invention.

5 It is also possible to use a copolymer, in which a dicarboxylic acid component such as isophthalic acid, naphthalene dicarboxylic acid, adipic acid, sebacic acid, or an alkyl ester derivative thereof and a glycol component such as propylene glycol, 1,4-butanediol,

10 cyclohexanedimethanol, neopentyl glycol, bisphenol A, or diethylene glycol are copolymerized, as a copolymer component within such a range as not to impair the workability and strength to a significant degree. The PES(D) is preferably the one that is dissolved in a mixed

15 solvent of 50% by weight of phenol and 50% by weight of tetrachloroethane so as to have an adequate intrinsic viscosity $[\eta]$ (unit, dl/g) of 0.5 to 1.5 when measured at 30 °C.

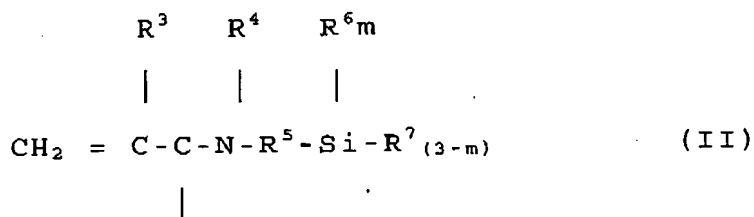
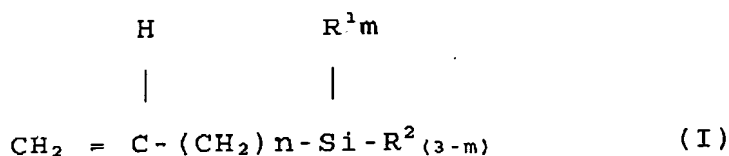
The EVOH resin (A) used in the present invention

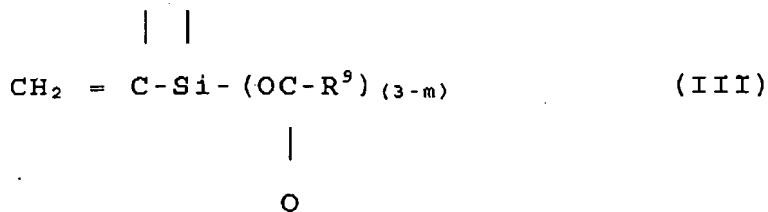
20 desirably has an ethylene content of 20% to 60 mol %, preferably 25% to 55 mol %. When the content of ethylene unit is less than 20 mol %, the melting point and the decomposition point of the EVOH resin come close to each other, which makes thermostability and melt moldability

25 poor. When the content of ethylene unit is more than 60 mol %, gas barrier properties are deteriorated, which is undesirable. The saponification degree of the EVOH

is desirably at least 95 mol %, preferably at least 98 mol %. When the saponification degree is less than 95 mol %, the thermostability is poor, and not only coloring occurs and gel and fish eye tend to occur during melt molding but also gas barrier properties are deteriorated, which is not desirable. Further, the content of vinylsilane compound unit in EVOH is from 0.0002 to 0.2 mol %. In this range, a large improvement in impact delamination resistance is observed. When this content exceeds 0.2, the EVOH (A) itself tends to gel, which is not good for use.

Here, the vinylsilane compound is an olefinic unsaturated monomer containing silicon, and one or more kinds selected from the compounds represented by the following general formulae (I), (II), and (III) can be suitably used.





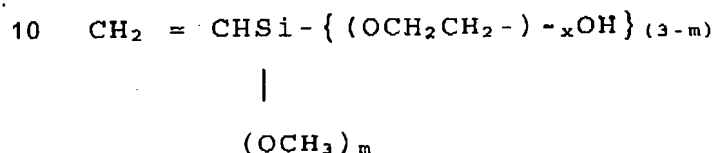
5 [where, n is 0 or 1; m is 0, 1, or 2; R¹ is a lower alkyl group, allyl group, or lower alkyl group having an allyl group; and R² is a branched or unbranched saturated alkoxyl group of 1 to 40 carbon atoms and the alkoxyl group may optionally have substituent
 10 containing oxygen. R³ is hydrogen or methyl group; R⁴ is hydrogen or a lower alkyl group; R⁵ is an alkylene group or a bivalent organic residue in which carbon-atom chains are interlinked via oxygen or nitrogen; R⁶ is hydrogen, halogen, a lower alkyl group, allyl group,
 15 or lower alkyl group having an allyl group; R⁷ is an alkoxyl group or acyloxyl group (where the alkoxyl group or acyloxyl group may have substituent containing oxygen or nitrogen); R⁸ is hydrogen, halogen, a lower alkyl group, allyl group, or lower alkyl group having an allyl
 20 group; and R⁹ is a lower alkyl group.]

In more detail, R¹ represents a lower alkyl group of 1 to 5 carbon atoms, allyl group of 6 to 18 carbon atoms, or lower alkyl group of 1 to 5 carbon atoms having an allyl group of 6 to 18 carbon atoms; R⁴ represents
 25 hydrogen or a lower alkyl group of 1 to 5 carbon atoms; R⁵ represents an alkylene group of 1 to 5 carbon atoms or a bivalent organic residue in which carbon-atom chains

are interlinked via oxygen or nitrogen; R^6 represents hydrogen, halogen, a lower alkyl group of 1 to 5 carbon atoms, allyl group of 6 to 18 carbon atoms, or lower alkyl group of 1 to 5 carbon atoms having an allyl group of 6 to 18 carbon atoms; R^7 represents an alkoxyl group of 1 to 40 carbon atoms or acyloxyl group (where the alkoxyl group or acyloxyl group may have substituent containing oxygen or nitrogen); R^8 represents hydrogen, halogen, a lower alkyl group of 1 to 5 carbon atoms, allyl group of 6 to 18 carbon atoms, or lower alkyl group of 1 to 5 carbon atoms having an allyl group of 6 to 18 carbon atoms; and R^9 is a lower alkyl group of 1 to 5 carbon atoms.

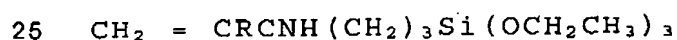
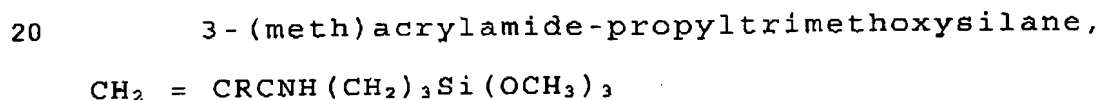
The olefinic unsaturated monomer containing silicon represented by the general formula (I) includes vinyltrimethoxysilane, vinylmethyldimethoxysilane, vinyl dimethylmethoxysilane, vinyltriethoxysilane, vinylmethyldiethoxysilane, vinyl dimethylethoxysilane, allyltrimethoxysilane, allylmethyldimethoxysilane, allyl dimethylmethoxysilane, allyltriethoxysilane, allyl dimethylethoxysilane, vinyltris (β -methoxyethoxy) silane, vinylisobutyldimethoxysilane, vinyl ethyldimethoxysilane, vinylmethoxydibutoxysilane, vinyl dimethoxybutoxysilane, vinyltributoxysilane, vinylmethoxydihexyloxysilane,

vinyl dimethoxyhexyloxysilane, vinyl trihexyloxysilane,
 vinyl methoxydioctyloxysilane,
 vinyl dimethoxyoctyloxysilane, vinyl trioctyloxysilane,
 vinyl methoxydilauryloxysilane,
 5 vinyl dimethoxylauryloxysilane,
 vinyl methoxydioleyloxysilane,
 vinyl dimethoxyoleyloxysilane, polyethylene glycol
 derivatives of vinyl methoxysilane represented by the
 general formula

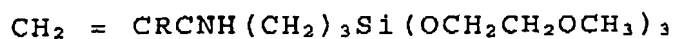


(where m is the same as described above and x represents
 1 to 20), and the like, and from economic standpoint,
 15 vinyl trimethoxysilane is preferred.

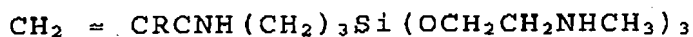
The olefinic unsaturated monomer containing
 silicon represented by the general formula (II) includes
 (meth)acrylamide-straight or branched chain
 alkyltrialkoxysilanes such as



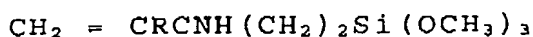
3-(meth)acrylamide-propyltri(β-methoxyethoxy)silane,



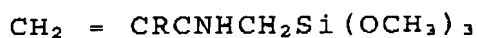
3-(meth)acrylamide-propyltri(N-methylaminoethoxy)silane,



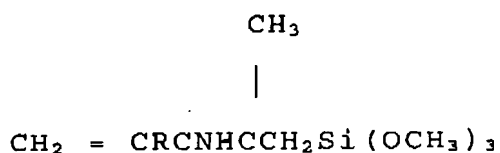
3-(meth)acrylamide-ethyltrimethoxysilane,



1-(meth)acrylamide-methyltrimethoxysilane,

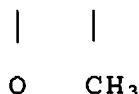


2-(meth)acrylamide-2-methylpropyltrimethoxysilane, and

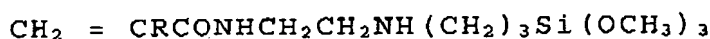


2-(meth)acrylamide-isopropyltrimethoxysilane

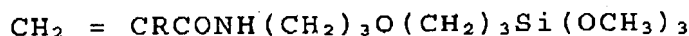




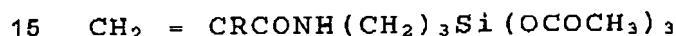
(where R represents hydrogen or a methyl group);
 (meth)acrylamide-nitrogen-containing or
 5 oxygen-containing alkyltrialkoxysilanes such as
 N-(2-(meth)acrylamide-ethyl)-aminopropyltrimet
 hoxysilane and



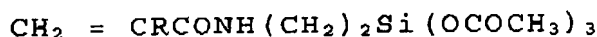
(3-(meth)acrylamide-propyl)-oxypropyltrimethox
 10 ysilane



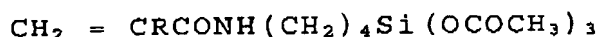
(where R represents hydrogen or a methyl group);
 (meth)acrylamide-alkyltriacyloxysilanes such as
 3-(meth)acrylamide-propyltriacetoxysilane,



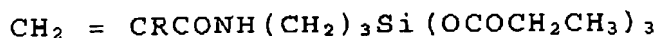
2-(meth)acrylamide-ethyltriacetoxysilane,



4-(meth)acrylamide-butyltriacetoxysilane,



20 3-(meth)acrylamide-propyltripropionyloxysilane



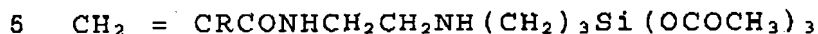
2-(meth)acrylamide-2-methylpropyltriacetoxysil
 ane, and

25 CH_3



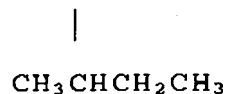
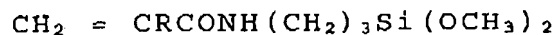
|
CH₃

N-(2-(meth)acrylamide-ethyl)aminopropyltriacetoxysilane



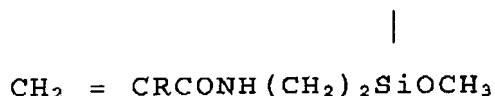
(where R represents hydrogen or a methyl group);
(meth)acrylamide-alkyldi- or monoalkoxy- or di- or monoacyloxysilanes such as

3-(meth)acrylamide-propylisobutyldimethoxysilane,
10 ne,

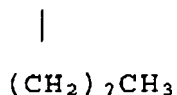
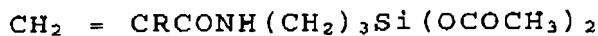


2-(meth)acrylamide-ethyldimethylmethoxysilane,

15 CH₃



20 3-(meth)acrylamide-ethyldimethylmethoxysilane,



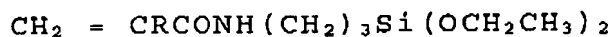
1-(meth)acrylamide-methylphenyldiacetoxysilane

25 ,

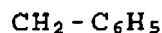




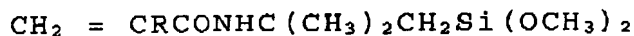
3-(meth)acrylamide-propylbenzyldiethoxysilane,



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2-(meth)acrylamide-2-methylpropylmonochlorodimethoxysilane, and



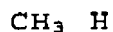
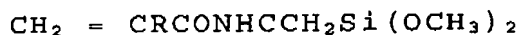
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2-(meth)acrylamide-2-methylpropylhydrogenmethoxysilane



15

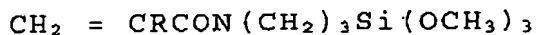


(where R represents hydrogen or a methyl group);

(N-alkyl-(meth)acrylamide)alkyltrialkoxo- or

20 triacetoxysilanes such as

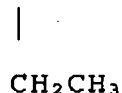
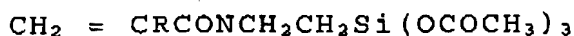
3-(N-methyl(meth)acrylamide)-propyltrimethoxysilane and



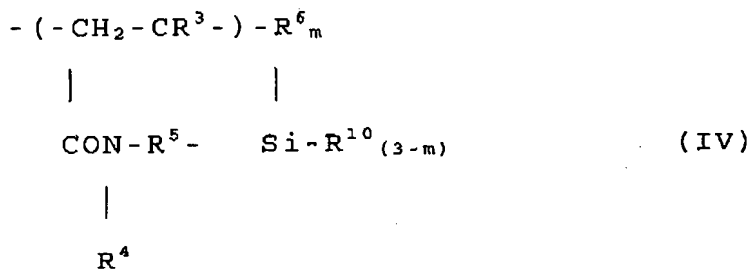
25



2-(N-ethyl-(meth)acrylamide)-ethyltriacetoxysilane



(where R represents hydrogen or a methyl group); and
 5 the like. Among these,
 3-(meth)acrylamide-propyltrimethoxysilane and
 3-(meth)acrylamide-propyltriacetoxysilane are
 relatively easily produced industrially and low in cost,
 and the amide bonds of
 10 2-(meth)acrylamide-2-methylpropyltrimethoxysilane
 and
 2-(meth)acrylamide-2-methylpropyltriacetoxysilane
 are markedly stable to acid or alkali; therefore these
 compounds are preferably used. A modified EVOH
 15 containing silicon that is obtained by copolymerizing
 the polymerizable silicon-containing monomer
 represented by the general formula (II) with vinyl
 acetate and ethylene, followed by saponification of the
 obtained copolymer, contains a copolymerization unit
 20 shown by the following general formula (IV):



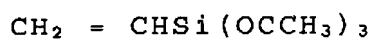
25 (where R^3 , R^4 , R^5 , R^6 , and m are the same as described
 above. R^{10} represents a hydroxyl group or a salt of

hydroxyl group represented by the general formula OM
(M represents an alkali metal or NH₂)).

The olefinic unsaturated monomer containing
silicon represented by the general formula (III)

5 includes

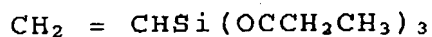
vinyltriacetoxysilane,



|

O

10 vinyltripropionyloxysilane,



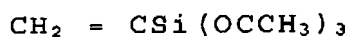
|

O

isopropenyltriacetoxysilane,

15 CH₃

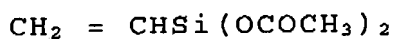
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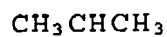
|

O

20 vinylisobutyldiacetoxysilane,



|



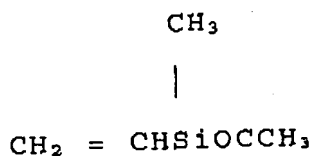
vinylmethyldiacetoxysilane,

25 CH₂ = CHSi(OCOCH₃)₂

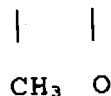
|



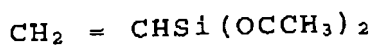
vinyl dimethylacetoxysilane,



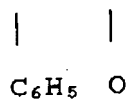
5



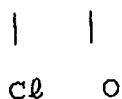
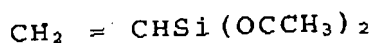
vinyl phenyldiacetoxysilane,



10

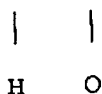
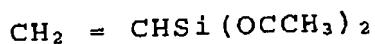


vinyl monochlorodiacetoxysilane, and



15

vinyl monohydrogendiacetoxysilane.



20 From economical point of view, vinyl triacetoxysilane is preferred.

The copolymerization of the olefinic unsaturated monomer containing silicon with vinyl acetate and ethylene is desirably carried out by solution polymerization in the presence of alcohol.

25 Further, the EVOH resin (A) of the present invention may be modified by other copolymerizable monomers within such a range as not to impair the object

of the present invention. These monomers for modification include propylene, 1-butene, 1-hexene, 4-methyl-1-pentene, acrylic acid ester, methacrylic acid ester, maleic acid, fumaric acid, itaconic acid, higher fatty acid ester, alkyl vinyl ether, N-(2-dimethylaminoethyl)methacrylamides or its quaternary derivatives, N-vinylimidazole or its quaternary derivatives, N-n-butoxymethyl acrylamide, and the like.

10 The EVOH resin (A) according to the present invention is one that has a melt index (MI), measured under the conditions of a temperature of 190 °C and a load of 2160 g according to the method described in JIS K6750, of 0.1 to 50 g/10 min, preferably 0.5 to 30 g/10 min, and particularly preferably 0.5 to 20 g/10 min. When this MI is less than 0.1 g/10 min, fluidity at the time of melt molding is poor, resulting in not only increases in extrusion load and injection load but also trouble in high speed continuous operation, and to make things worse, gel and fish eye tend to occur, all of which are not desirable. Further, when the MI exceeds 50 g/10 min, not only do the drop strength and the impact strength of a molded container decrease but also the injection amount of EVOH into each metal mold in a multicavity blow molding machine is not stabilized, resulting in difficulty in uniform container molding, and to make things worse, the thickness distribution

of the EVOH in a multilayer injection molded preform in the axial direction becomes nonuniform, and the thickness distribution of EVOH in the direction perpendicular to the axis tends to become thicker in the mouthpiece for the preform, showing a tendency to become apparently opaque in the mouth portion, none of which is not desirable.

For the resin (B) blended with the EVOH resin (A) used in the present invention, there are thermoplastic resins that satisfy the formulae (I) to (IV), preferably the following formulae (I') to (IV'):

$$3 \leq MI(B)/MI(A) \leq 190 \quad (I')$$

$$MP(B) \leq MP(A) - 20 \quad (II')$$

$$CH(A) \leq CH(B) - 5 \quad (III')$$

$$DS(A) \geq DS(B) \quad (IV')$$

When $MI(B)/MI(A)$ is smaller than 1 or when $MP(B)$ is higher than $MP(A)$, delamination caused by impact on a molded container is easy to occur. On the other hand, when $MI(B)/MI(A)$ is equal to or larger than 200, the thickness distribution of the EVOH composition layer (C) becomes nonuniform, which is undesirable. When $MI(B)/MI(A)$ and the difference between $MP(B)$ and $MP(A)$ are larger within the conditions that satisfy the formulae (1) and (2), impact delamination resistance is better. Further, when $CH(A)$ is smaller than $CH(B)$ or when $DS(A)$ is larger than $DS(B)$, delamination due to impact is also easy to occur. Furthermore, as the

difference of CH(B) from CH(A) and the difference of DS(A) from DS(B) become larger, impact delamination resistance is better. Still further, it is important to select resins that meet the above formulae (I) to (IV), preferably (I') to (IV') as the resin (B), and these resins include ethylene-vinyl acetate copolymer, saponified ethylene-vinyl acetate copolymer, and further, modified copolymer thereof. A carboxyl-modified copolymer in which 0.0001 to 1 mol %, preferably 0.001 to 0.1 mol % of maleic anhydride or the like is grafted to an ethylene-vinyl acetate copolymer or a saponified ethylene-vinyl acetate copolymer for modification as well as a blend of 90 to 10 parts by weight of the modified copolymer and 90 to 10 parts by weight of the ethylene-vinyl acetate copolymer or the saponified ethylene-vinyl acetate copolymer, or both further improve impact delamination resistance, and therefore are particularly effective.

An appropriate blend ratio of the EVOH (A) to the resin (B) is 100 parts by weight of the EVOH (A) to 5 to 40 parts by weight of the resin (B), preferably 7 to 30 parts by weight. When the blend amount of the resin (B) is less than 5 parts by weight, delamination caused by impact on a molded container tends to occur. Further, when the blend amount of the resin (B) is more than 40 parts by weight, gas barrier properties are undesirably reduced.

The method of blending the resin (A) with the resin (B) is not particularly limited and includes a method in which the resin (A) and the resin (B) are dry-blended and used as it is, a method in which the dry-blended pellets are repelleted by subjecting to a Banbury mixer and a uniaxial extruder or a biaxial extruder, followed by drying, and the like. At the time of blending, it is an option to add an antioxidant such as hindered phenol, hindered amine, or metallic soap, a UV absorbing agent, or a coloring agent within such a range as not to impair the object of the present invention, and their addition is effective.

As a means of further improving impact delamination resistance of a coinjection stretch blow molded container, it is more effective to use a resin in which 1 to 20 parts by weight of the resin (B) is blended with 100 parts by weight of the thermoplastic polyester resin, that is, to blend the resin (B) with both of the PSE and the EVOH. When the addition amount of the resin (B) to the PSE is equal to or less than 1 part by weight, the improvement effect is less, and when the addition amount is equal to or more than 20 parts by weight, the strength of a bottle is reduced, and a defect in appearance of the bottle occurs, which is not desirable.

A precursor of a container (parison) having a multilayer structure can be obtained, in one clamping operation of a molding machine having two injection

cylinders, by injecting molten polyethylene terephthalate and the EVOH resin composition (C) into a single metal mold alternately from each injection cylinder with staggered timing or at the same time from a concentric nozzle, or both. For example, the precursor of the container is obtained by a common method for obtaining a parison with bottom with its inner layer being completely enclosed by the innermost and outermost PES layers where an intermediate layer is formed by arranging initially injected PES on the inner and outer surface layers and a later injected EVOH composition (C) layer or PES, or both in the inside of the initially injected inner and outer PES layers, and further in some cases, injecting again the EVOH composition (C) or PES, or both, and the method is not particularly limited from a facility viewpoint. The multilayer parison in a warm state is heated directly or with a heating element such as block heater or infrared heater to 75 to 150 °C, subsequently sent to a stretch blow process, stretched one to five fold in the longitudinal direction, and then blown one to four fold with compressed air or the like, and the PES or the EVOH composition, or both are stretched uniaxially or biaxially, thereby providing a stretch blown multilayer polyester container. The heating and stretching process is also not limited from a facility viewpoint.

Whether the stretch blown container is subjected

to heat treatment or not is significantly related to impact delamination of the multilayer bottle. Herein, it is desirable to satisfy the following formula (4):

$$(T_p - 20) > T_c > T_B \quad (V)$$

5 where T_p is the melting point of PES ($^{\circ}\text{C}$),
 T_c is the heat treatment temperature of a container ($^{\circ}\text{C}$), and

T_B is the melting point or the softening point of the resin (B) ($^{\circ}\text{C}$).

10 When T_c is higher than $T_p - 20$, the bottle strength becomes poor possibly because the outermost PES layer is softened to decrease stretch orientation. On the other hand, when T_c is lower than T_B , improvement in impact delamination resistance of the multilayer
15 container is not observed. The heat treatment time is desirably from approximately 1 to 100 seconds, and the method of heat treatment is not particularly limited, but generally includes a method of increasing the
20 temperature of metal mold in the blow process, a method of treating with heat by reintroducing into a heated metal mold under pressure, a method of heat treatment with hot-air heat medium, or the like. Further, when a high temperature bottle is taken out after the heat treatment, a method of rapid cooling of the heated metal
25 mold or the heat medium, a method of cooling with a cooled metal mold by reintroducing into a cooled metal mold under pressure, or the like is listed.

The multilayer container of the present invention is structured such that, using two kinds of resins, the PES and the EVOH composition, intermediate layers containing one or more EVOH composition layers or one
5 or more layers of each of the EVOH composition and the PES are completely enclosed by the innermost and outermost PES layers, and generally includes PES/EVOH composition/PES, PES/EVOH composition/PES/PES, and PES/EVOH composition/PES/EVOH composition/PES
10 structures and the like. With respect to the thickness of parison, the total thickness is from 2 to 5 mm, and the EVOH composition layers are from 10 to 500 μ in total. In general, as the EVOH layer is thinner and the number of the EVOH layers is smaller, and further as the position
15 of an EVOH composition layer near the outer layer side is closer to the outer layer surface, delamination caused by impact on a container is easier to occur. In addition, the total thickness of the body portion of a container is usually from 100 μ to 3 mm and is properly chosen
20 depending on use. The total thickness of the EVOH layers at this time is from 2 to 200 μ , preferably from 5 to 100 μ . Hereinafter, the present invention is further explained by way of examples, but not limited to these examples.

25

F. Examples

Example 1

As a thermoplastic polyester resin, polyethylene terephthalate having an intrinsic viscosity of 0.71 was used. As the EVOH composition (C), 20 parts by weight of the saponified ethylene-vinyl acetate copolymer resin (B) having an ethylene content of 72 mol %, a saponification degree of 80%, MI(B) of 73 g/10 min, and MP(B) of 69 °C was dry-blended with 100 parts by weight of the EVOH (A) having an ethylene content of 32 mol %, a saponification degree of 99.6%, vinylmethoxysilane in 0.04 mol %, MI(A) (melt index; 190 °C, 2160 g) of 1.3 g/10 min, and a melting point (MP(A)) of 181 °C, and pelleted with a biaxial extruder of 40 mmφ at 220 °C, followed by drying in vacuum for 16 hours at 80 °C. The conditions of this case were MI(B)/MI(A)=46 and 60<MP(B)=80 °C <MP(A)=181 °C. Using these resins, coinjection stretch blow molding was performed with a coinjection stretch blow machine of Nissei ASB Machine Co., Ltd. (Model 50-HT, 750 ml, two cavity mold) at a temperature of 270 °C at the end of the extruder on the PET side, at a temperature of 200 °C at the end of the extruder on the EVOH side, and at a temperature of 260 °C in a hot runner block part where the PET and the EVOH join, and a multilayer coinjection stretch blow molded bottle whose average thicknesses in the body portion were 90 μ for the inner PET layer, 20 μ for the intermediate EVOH composition layer, and 190 μ for the outer PET layer was obtained. At this time, the adhesion strength (T

type peeling strength) in the body portion of the bottle was as small as 30 g/10 mm breadth. In the body portion of the bottle, roughness having depths of 1.0 mm, 2.0 mm, and 4.0 mm over an area of 50 mm length and 15 mm width was provided so that impact delamination might easily occur. When the multilayer bottle filled with water was repeatedly dropped at atmospheric pressure from a height of 1 m with its body portion being horizontal, delamination occurred after dropping 13 times. Further, when the bottle was repeatedly dropped under pressure with 4 gas volumes of CO₂, delamination occurred after dropping 23 times. When this container was heat-treated for 30 sec by setting the temperature of blow metal mold to 120 °C at the time of stretch blowing from a parison, delamination occurred after dropping 24 times in the case of filling at atmospheric pressure and delamination did not occur even after dropping 50 times or more in the case of filling under pressure with CO₂ gas in the above delamination test, which proved improvement of impact delamination resistance by heat treatment. The results are shown in Table I.

Example 2

The resin (B) in Example 1 was replaced by one in which 60 parts by weight of saponified ethylene-vinyl acetate having an C₂H₄ content of 78 mol % and a saponification degree of 70% was blended with 40 parts by weight of ethylene-vinyl acetate having an C₂H₄

content of 78 mol % and graft modification with maleic anhydride of 0.02 mol % and pelleted with a uniaxial extruder, and an experiment was carried out as in Example 1. As the result, this container has an excellent impact delamination resistance as shown in Table I.

Example 3

The coinjection molding conditions in Example 1 were changed, where a two kind-five layer bottle having average thicknesses in the body portion of PET 90 μ /EVOH composition 10 μ /PET 100 μ /EVOH composition 10 μ /PET 90 μ in order from the inside was obtained. In this container, delamination occurred after dropping 12 times in the case of filling with water at atmospheric pressure, and delamination occurred after dropping 20 times in the case of filling under pressure with CO₂ gas. Further, when heat treatment was carried out as in Example 1, delamination occurred after dropping 20 times in the case of filling with water at atmospheric pressure, and delamination did not occur even after dropping 50 times or more in the case of filling under pressure with CO₂ gas.

Example 4

In Example 1, a polyester composition in which 10 parts by weight of the resin (B) was blended with 100 parts by weight of the polyester resin and pelleted was used, and an experiment was carried out as in Example 1. As the result, delamination occurred after dropping

13 times in the case of filling with water at atmospheric pressure, and delamination occurred after dropping 45 times in the case of filling under pressure, which proved improvement of impact delamination resistance by
5 blending the resin (B) with the polyester resin.

Examples 5 to 7

Using the compositions shown in Table I, experiments were carried out as in Example 1. The performances of the obtained bottles are shown in Table
10 I.

Comparative example 1

Using an EVOH resin not containing the thermoplastic resin (B) in Example 1, an experiment was carried out as in Example 1. As the result, in the
15 container, delamination occurred after dropping twice in the case of filling with water at atmospheric pressure, and delamination occurred after dropping 5 times even in the case of filling under pressure with CO₂ gas. Further, when the delamination test was performed with
20 the bottle treated with heat as in Example 1, delamination occurred after dropping once in the case of filling with water at atmospheric pressure, and delamination occurred after dropping 3 times even in the case of filling under pressure with CO₂ gas. Thus,
25 the effect of heat treatment was not observed.

Comparative example 2

Using the same polyester resin, resin (B), and EVOH

15 Comparative example 3

34



Table 1

	Raw resin																			
	Thermoplastic resin (B)																			
	EVOH (A)																			
	Bottle performance																			
	CaH ₄ content mol %	SI variation mol %	Saponification degree %	MI(A) g/10 min	MP(B) °C	Saponified ethylene-vinyl acetate copolymer		Ethylene-vinyl acetate copolymer (EVA)	MI(B) g/10 min	MI(B)/MI(A)	MP(B) °C	Blending amount Part by weight	No heat treatment Delamination test			No heat treatment Delamination test			Thickens of EVOH layer in body portion of bottle	
						CH ₃ content	Saponification degree						At atmospheric pressure Times	Under pressure with CO ₂ Times	At atmospheric pressure Times	Under pressure with CO ₂ Times	At atmospheric pressure Times	Under pressure with CO ₂ Times	Average (μ)	R(μ)
Example 1	32	0.04	99.6	1.3	181	72	80	-	73	56	69	20	13	23	24	50<	22	4		
"2	32	"	99.6	1.3	181	78	70	Maleic anhydride modified EVA	73	56	69	"	17	30	29	50<	21	3		
"3	32	"	99.6	1.3	181	72	80	-	73	56	69	"	12	20	20	50<	24	4		
"4	"	"	"	"	"	"	"	"	"	"	"	"	13	45	35	50<	25	4		
"5	44	0.02	99.6	5.5	165	72	80	-	73	13	69	20	13	24	27	50<	23	2		
"6	"	"	"	"	"	"	"	"	"	"	"	10	10	18	20	80<	22	5		
"7	32	"	99.6	1.3	181	68	60	-	60	46	45	20	15	23	28	50<	24	3		
Compara- tive example 1	32	"	99.6	1.3	181	Not blended		-	-	-	-	0	2	5	1	3	23	24		
"2	"	"	"	"	"	72	80	-	73	56	69	0	2	4	2	4	25	26		
"3	"	"	"	"	"	"	"	"	"	56	"	20	2	5	2	5	23	12		
"4	"	"	"	"	"	27	80	-	68	50	160	20	2	4	1	3	22	22		
"5	"	0	"	"	"	72	80	-	15	11	80	20	3	5	2	5	24	10		

Note: R = Maximum thickness minimum thickness in body portion of bottle